#### ADVANCED MATERIALS AND CHEMICALS

NatureWorks LLC (formerly Cargill, Inc.)

### Improving Biodegradable Plastics Manufactured from Corn

Since its invention in the 1930s, plastic packaging has posed two challenges: its dependence on petroleum and the problem of waste disposal. By the 1990s, both problems were considered serious; however, biodegradable plastics made from polylactic-acid-based polymers (PLA) derived from plants could provide the solution. In manufacturing, PLAs consume much less energy than plastics using petroleum-based feedstocks, and they decompose much faster than do petroleum-based plastics. However, PLA products lacked resistance to higher temperatures; for example, a hot-beverage drinking cup would distort when filled with a hot liquid. In addition, PLA plastic parts were expensive to manufacture, partly due to the additives necessary to improve the hardening time and other properties of the plastic resin used to make the products.

Cargill, Inc. was an agriculture company that had been researching plant-derived plastics. They proposed to improve plastics made of corn-based PLA by making them easier to manufacture and more heat resistant. Their comprehensive research approach required advances in polymer blends, additives, and manufacturing techniques and involved high technical risk, so the company needed outside funding. In 1994, Cargill applied for and received Advanced Technology Program (ATP) funding for a three-year project that started in 1995.

With ATP funding, Cargill reduced the hardening time for products made from PLA. Dow Chemical provided expertise in plastics manufacturing. At the conclusion of the project, they were still working on ways to increase heat resistance for the highest temperature foods that would be served in PLA products. Cargill and Dow formed Cargill Dow Polymers LLC (CDP) in 1997 and continued the development of NatureWorks, a PLA made from corn. The new company opened a major PLA manufacturing plant based on this technology in 2002. In 2005, Dow made a strategic decision to withdraw from the partnership. Cargill bought Dow's share and renamed the business "NatureWorks LLC," continuing to enhance and sell PLA resin for renewable-resource-based plastics.

As of 2006, NatureWorks was selling resin to more than 100 manufacturing partners worldwide for products ranging from food containers to apparel fibers. NatureWorks markets its PLA resin as a way to conserve expensive petroleum resources and reduce feedstock cost. The strongest markets have been in Europe and China; U.S. markets have also been growing. The project received extensive press coverage, four patents, and five awards or industry citations. The researchers have written numerous articles in trade publications and peer-reviewed journals.

#### COMPOSITE PERFORMANCE SCORE

(based on a four star rating)

\* \* \* \*

#### **Bio-Plastics Need Improvement**

Disposable plastics derived from petroleum have proliferated throughout the global economy since their usefulness was discovered in the 1930s. However, the large volume of plastics has created a significant disposal problem, because conventional plastics can take as long as 300 years to degrade in a landfill. More recently, the feedstock for plastic has become more expensive as the global demand for petroleum has grown. In response to these two challenges, scientists have been looking for renewable-resource-based plastic feedstocks.

The feedstock for plastic has become more expensive as the global demand for petroleum has grown.

Through the mid-1990s, researchers around the world made significant technological advances in the production of biodegradable plastic, but none were able to overcome the high cost of manufacturing commercial-grade quantities. One company, for example, developed a biodegradable plastic called Biopol that Monsanto was interested in marketing. However, with manufacturing costs between \$5 and \$15 per pound, the product was not competitive with existing plastics. Monsanto eventually sold its interest in Biopol to Metabolix, where researchers are continuing to develop a commercially viable product.

### Cargill Proposes to Manufacture Better, Cheaper Bioplastics

In 1989, Cargill, an international processor and distributor of agricultural, food, and industrial products, began researching plastics manufacturing using plants as feedstocks. The company had already invested \$8 million of its own funds and had filed 30 patent applications related to producing lactic acid, forming resin pellets, and evaluating polymer architecture (the qualities of resin). They were looking for ways to expand the use of corn and related byproducts moving through their mills. They believed that they could develop the technology to optimize polymer blends, additives, and manufacturing techniques and reduce

the cost of producing renewable resource-based plastic to about \$1 per pound. The company's proposed research was complex and technically risky. Cargill's approach would evaluate the effects on degradability at every step in the development process. In 1994, Cargill applied for a three-year single company award from ATP to develop the fundamental methodology for improving the performance characteristics of cornbased plastics to make them more competitive in the United States. The project began in early 1995.

In addition to reducing the per-pound cost of plastics production, Cargill would determine the fundamental structure/property relationships for polylactic-acid-based polymer (PLA) and then use that understanding to develop new polymer-processing technologies. The goal was to improve the PLA's performance properties. At the time of the ATP-funded project, biodegradable plastics lacked the heat resistance necessary for food service items (for example, a cup must not distort when used for hot beverages).

Most plastics start with a petrochemical feedstock. Cargill wanted to improve a PLA polymer derived from plant sugars, at first corn. (A polymer consists of organic molecules, usually from coal or petroleum.) Plants create carbon during photosynthesis and store it in starches. Cargill first milled the corn to separate the starches. They used bacteria to ferment the sugar, similar to processing wine or beer. The fermentation creates lactic acid, which then can bind together to form a polylactide polymer chain.

PLA was a good candidate for further improvement. Cargill's prior investments in the PLA manufacturing process had lowered the cost, and the product already resisted some hot liquids. PLA provided other desirable characteristics. For example, a candy wrapper made of PLA stays folded when twisted and forms an effective barrier against food aromas, grease, and oils. These wrappers have a high gloss and clarity that customers seem to prefer over the more common polyethylene terephthalate (PET) and polystyrene wrappers.

Cargill planned to produce PLA resins in various grades to be sold to "converters," companies that melt the resin to manufacture fiber for bedding and apparel, plastic film for packaging and agricultural use, containers molded by injection (such as milk bottles), and numerous other products. If successful, Cargill expected to produce one billion pounds of PLA polymer resin annually. Finished products would be renewable, recyclable, and compostable.

Cargill realized early in the ATP-funded project that it needed a partner with credibility in the plastics industry. Therefore, in 1996, the company formed a collaboration with Dow Chemical to further develop the PLA resins. Dow brought critical knowledge of polymer science to the project.

### Availability of Low-Cost Lactic Acid Is Critical in Developing PLA

One of Cargill's first tasks was to evaluate and improve the properties of PLA by using differing crystallization processes and additives to streamline the manufacture of distinct grades of resin. Early expected applications of corn-based plastic products to be made from PLA resins included the following:

- Compostable bags made of thin plastic sheeting (called "film") for food and yard waste
- Plastic wrap for food packaging
- Fiber and nonwoven products, such as agricultural mulch bags, medical garments, and twine
- Rigid container packaging, such as food cartons, bag and box coatings, and drinking cups made by injecting the plastic into molds (for example, yogurt containers)

Cargill's second technical task was to enhance the functional properties of PLA resins by reducing the hardening times of the products manufactured. For example, a utensil is formed by injecting a mold with liquid plastic prepared from molten resin. The product solidifies from a viscous liquid to a rigid or semi-rigid form. If a product has hardened enough to be removed from the mold without distortion, the hardening time is deemed sufficient. To be economically viable, this time needed to be only a few seconds. When the project began, the hardening time for PLA injection-molded containers was about a minute.

To decrease this hardening time, the researchers needed a nucleant, or hardening accelerator, that did not significantly reduce the product's rate of degradability. Mineral talc met this test, but it reduced the clarity of PLA sheet, which is used in thermoformed clear food packaging such as deli containers. By adding talc, researchers achieved hardening times of eight seconds. Cargill would later sell this grade of PLA resin

(pellets) to converters with markets for products that did not require high clarity. Existing converters and manufacturers depended on petroleum-based resins. Switching to PLA would require that the converters make significant process changes.

At full capacity, the NatureWorks plant can consume 40,000 bushels of corn daily to produce polylactic-acid-based polymers.

The third major technical task was to evaluate the relationship of each chemical and processing change to the rate of degradability.

The University of Minnesota assisted with nuclear magnetic resonance studies to help Cargill more clearly understand the physical structure of the polymer molecule and changes rendered by various hardening accelerators. In addition to the University of Minnesota, several other subcontractors and partners assisted with various tasks:

- Pennsylvania State University (crystallization rate)
- California Tech (hardening process)
- University of Tennessee (PLA and fiber formation studies, a breakthrough in understanding polymer properties and their control)
- Fiber Science (process development for fiber spinning)
- Scott Gessner and Associates (fiber/nonwoven applications, such as mulch bags, twine, and medical garments)
- Nangeroni and Associates (thermoforming applications, such as food service clamshell boxes)
- Organic Waste Systems (PLA decomposition testing in compost)
- Technology Management Group (technical reporting, consulting)

In 1997, Cargill and Dow formed a new company called Cargill Dow Polymers LLC (CDP) to continue work on the ATP-funded research. CDP was researching ways to shorten PLA's hardening time and increase heat resistance; at that time, prototype plastic knives, forks, and spoons made from PLA could only be used with cold food.



Figure 1. CDP's NatureWorks PLA plant began operations in 2002. At fully realized capacity, it can produce 140,000 metric tons (300 million pounds) per year and consume up to 40,000 bushels of corn daily.

#### **CDP Markets and Commercializes PLA**

When ATP funding ended in January 1998, Cargill provided an early demonstration of PLA products at the 1998 Winter Games in Nagano, Japan. Cargill sponsored a fashion show of "clothes from the earth," which included fabrics made from PLA resin. By 1999. CDP announced that it had produced a polymer from 100-percent renewable corn-based resources, called "NatureWorks PLA". The patented process uses 30- to 50-percent less fossil fuel than conventional petroleumbased plastics, even when considering the energy consumed when producing the corn. In addition, because the growing plants consume atmospheric carbon dioxide (a primary greenhouse gas), overall emissions are more than 50-percent lower than conventional plastics. Patrick Gruber, former vice president and chief technology officer of CDP, said, "We broke a paradigm in the chemical industry. We have combined very inexpensive large-scale fermentation with chemical processing to bring a valueadded polymer product to the marketplace that improves the environment as well."

CDP formally launched the product, NatureWorks PLA, in 2000, with several commercial grades for specific applications. Cargill and Dow invested more than \$300 million in a large-scale PLA plant in Blair, Nebraska, which came online in 2002. This facility has a name-plate capacity of 140,000 metric tons per year (see Figure 1). The target PLA resin price was 50 cents to \$1 per pound, to primarily be at parity with PET. CDP collaborated with the U.S. Grains Council to open international markets for PLA. The Department of Energy funded further CDP research to enhance the catalyst used to produce lactic acid and improve overall process efficiency.





Figure 2. Left: sample Ingeo fiber-based carpet marketed by Interface Fabrics Group (http://www.interfacesustainability.com/biobased.html).

Right: sample wool/Ingeo fiber blend blankets marketed by Faribault Mills.

At full capacity, the NatureWorks plant can consume 40,000 bushels of corn daily to produce PLA. While the plant uses corn as its feedstock, the company plans to develop future processes using other raw materials, such as wheat and sugar beets. Furthermore, CDP planned to invest \$250 million for research in processing bio-waste, such as corn stalks and rice hulls. The scale of CDP's investment spurred several competitors to develop bioprocesses for polymers and other chemicals from renewable resources, among them Celanese, Chevron Research and Technology, DuPont, Procter & Gamble, and Toyota.

In addition to biodegradable plastics, CDP said that PLA-based fibers could compete in cost and performance with conventional polyester, nylon, cotton, and silk. Brent Erickson, of the Biotech Industry Organization, predicted that "[NatureWorks PLA] could transform the old economy. It's going to provide new ways to make things that are cleaner and more economical." CDP had invested \$750 million in PLAbased fibers. In 2002, the U.S. Federal Trade Commission agreed to designate these fibers as a new generic fiber, Ingeo.<sup>2</sup> Ingeo can be made fine (less than 1.0 denier, suitable for lingerie) or heavier for fiber spinning and weaving (see Figure 2). Its advantages include high extrusion and spin speeds and reduced processing temperatures, leading to reduced energy consumption. Ingeo fiber based fabrics offer low moisture absorption, rapid wicking of moisture away from the skin, low flammability, soil and stain resistance, wrinkle resistance, softness, ultraviolet light resistance (which minimizes color fading), and light weight. Early PLA resin customers for fiber applications included Fiber Innovations Technology (FIT), Parkdale Mills, Interface Inc., and Unifi Inc.

After CDP had developed marketable resins for some commercial products, the company pursued licensing

<sup>&</sup>lt;sup>1</sup>Chea, Terence. "From Fields to Factories: Plant-Based Materials Replace Oil-Based Plastics, Polyesters," Washington Post, May 3, 2002.

<sup>&</sup>lt;sup>2</sup> Ingeo is a NatureWorks registered trademark.



Figure 3. Sample food service containers made from renewable PLA.

arrangements. In April 2003, CDP signed an agreement with Toray Industries, one of the world's largest fiber and textile producers.<sup>3</sup> The license permitted Toray to produce and sell Ingeo fibers and fiber products. CDP also had an agreement with Pacific Coast Feather Company to sell Ingeo fiberfill bedding (for pillows, comforters, and the like) at several major retail outlets.<sup>4</sup> At the same time, Ingeo was marketed as carpeting and textiles through Interface Flooring Systems, Lees Carpets, Milliken, Quaker Fabric Corp., Faribault Mills, and Valdese Weavers.

PLA resins are also used to manufacture film and packaging to replace PET and cellophane (see Figure 3). Cellophane is made from wood pulp; the feedstock costs more than corn and its manufacturing process is more complex. CDP's early customers for packaging included Biocorp Inc. (cold-drink cups), Dunlop (golf ball packaging), Autobar (European food packaging), and Trespaphan (European packaging). Coca Cola used CDP's NatureWorks PLA cups at the 2002 Olympic Winter Games in Utah. Wild Oats Markets Inc. in the Pacific Northwest became the first U.S. grocery store chain to offer PLA-based packaging, called "Corntainers," at an initial cost of 40- to 50-percent more than plastic. Wild Oats operates a commercial composting facility for PLA packaging. Extensive testing for the International Organization for Standardization

(ISO), the American Society for Testing and Materials (ASTM), and other organizations has shown that when composted commercially, select parts such as a drinking cup made from PLA biodegrades fully in 47 days.

Yellow corn is abundant. In the United States, it is overproduced by about 10 percent annually. NatureWorks consumes slightly less than 0.5 percent of this surplus.<sup>5</sup> (By comparison, 1.2 percent of U.S. corn is used to produce alcohol, and 55.5 percent is fed to animals.<sup>6</sup>) PLA also uses 30- to 50-percent less fossil fuel than conventional plastics.

#### **Bio-Plastics Market Burgeons**

The annual global production of plastics (the vast majority derived from petroleum) totaled more than 120 million metric tons in 2000. Initial demand for PLA came from the Asia Pacific Rim and Europe, where it helped meet environmental requirements. According to Jim Hobbs, Product Director for NatureWorks, "Waste disposal is a bigger issue in Japan... NatureWorks plastic is a natural for them because it can be composted and, if it gets incinerated [as much of their trash does], it burns with very low levels of emissions." The Japanese eco-business market, which includes biodegradable plastics, reached \$251 billion in 2000 and is projected to reach \$410 billion in 2010.

The U.S. market is comparatively small but growing. The Freedonia Group estimated the U.S. market for degradable plastics at 115,000 metric tons, at a value of \$330 million, in 2004, with projected annual growth of 13.7 percent, reaching 170,000 metric tons (\$490 million) in 2008. PLA is projected to represent 36 percent of that market. As of mid-2006, NatureWorks volume was divided in thirds across three geographies: Asia Pacific, Europe and North America.

#### **Dow Sells Its CDP Share to Cargill**

Using CDP's PLA to manufacture plastics was still more expensive than manufacturing conventional plastics. As

<sup>&</sup>lt;sup>3</sup> "Cargill Dow and Toray Team Up on Ingeo," Cargill Dow Fiber News, April 25, 2003.

<sup>&</sup>lt;sup>4</sup> Sloan, Carole. "NatureWorks Hits Retailers' Shelves," *Home Textiles Today,* Vol. 23, No. 40, p. 2, June 10, 2002.

<sup>&</sup>lt;sup>5</sup> "Four Plastics Companies Commit to Biodegradable Plastics," Environment News Service, February 16, 2004.

http://www.ens-newswire.com/ens/feb2005/2005-02-16-04.asp

<sup>&</sup>lt;sup>6</sup> Feed Outlook, U.S. Department of Agriculture, Economic Research Service, January 17, 2006. http://www.ncga.com/WorldOfCorn/main/consumption1.asp

<sup>&</sup>lt;sup>7</sup> Verespej, Michael A. "Polylactide Polymers." *Industry Week*, Vol. 249, No. 20, pp. 67-68, December 11, 2000.

<sup>&</sup>lt;sup>8</sup> "Developing Products that Protect the Environment: The Real Deal." <a href="http://www.cargill.com/about/citizenship/developingproducts.htm">http://www.cargill.com/about/citizenship/developingproducts.htm</a>

<sup>&</sup>lt;sup>9</sup> "Attractive Sectors: Environment." Japan External Trade Organization, http://www.jetro.go.jp/en/market/attract/environment/env.pdf, November 2005.

<sup>10 &</sup>quot;Degradable Plastics to 2008." Group 2004, http://www.freedoniagroup.com/pdf/1866smwe.pdf.

a result, CDP sales were slower than anticipated, but growing. The cost of PLA declined from \$1 per pound in 2002 to less than 85 cents per pound by 2004 (less for large-volume, long-term contracts). However, sales rose 60 percent in the first nine months of 2004, and CDP had more than 1,500 grocery stores selling products packaged in PLA and more than 3,000 retail stores carrying Ingeo fiber products.

NatureWorks leads the field in producing and developing polymers from renewable resources.

Despite CDP's sales growth, Dow Chemical made a strategic decision to withdraw from the partnership in January 2005. Cargill bought Dow's 50-percent share of the partnership and changed the name of the PLA resin manufacturing business to NatureWorks LLC. Subsequently, they changed their market strategy to emphasize freedom from petroleum, rather than biodegradability. The rising price of oil may help NatureWorks find markets for PLA, especially in European, Chinese, and other Asian markets, which are interested in PLA as an alternative to petroleum-based resin products. For every \$5-per-barrel increase in the cost of oil, PLA gains a price advantage over PET of 1 cent per pound. The price per barrel of oil has risen from approximately \$17 in 1995 to \$60 in 2006.

NatureWorks leads the field in producing and developing polymers from renewable resources. The company is continuing to improve the properties of the PLA polymer and reduce its production cost. In 2005, they led a project to build a pilot biorefinery to produce lactic acid and ethanol from alternative sources, such as corn stalks and leaves. They are collaborating with Genencor International and logen Corporation on this project. NatureWorks was also one among six research and development projects funded by the U.S. Department of Energy (DOE) to use agricultural crop wastes for biocatalytic conversion in place of conventional chemical and energy processes. DOE provided \$26 million to support technologies that could convert 25 percent of chemical manufacturing to an agricultural feedstock base by 2030.11

#### **NatureWorks Continues to Grow**

As of 2005, the PLA resin grades produced by NatureWorks for sale to converters included the four original project research areas (thin film, plastic wrap, fiber and non-wovens, and rigid containers). NatureWorks claims sales to hundreds of global manufacturing partners, as described on their website http://www.natureworksllc.com. These manufacturing partners range from industries in food packaging to fiber producers, who have discovered that adding PLA to natural fiber production provides higher performance than all-natural material. Below is a sample of NatureWorks' manufacturing customers:

- Brenmar Company is an authorized distributor of the NatureWorks PLA line of products, including the VersaPak clear packaging product line for deli, bakery, and produce (depicted previously in Figure 3). Brenmar also offers NatureWorks PLA products such as plates, cutlery, and cold-drink cups with lids (see http://www.brenmarco.com).
- Wilkinson Manufacturing produces clear food packaging under the brand name "NaturesPLAstic" (see <a href="http://www.wilkinsonindustries.com">http://www.wilkinsonindustries.com</a>).
- Wild Oats Markets Inc. offers PLA-based packages and composts them in a commercial facility.
- Pacific Coast Feather Company manufactures comforter and pillow fiber filling; their products are carried widely by Bed Bath and Beyond, Linens N Things, Macy's stores, and others.
- Coca Cola Company uses soft drink cups that contain PLA.
- Interface Flooring Systems produces a residential carpet product created from Ingeo fiber.
- Wal-Mart uses a variety of PLA food containers.
   After a year-long test of PLA plastic, Wal-Mart implemented new packaging for strawberries, cut

<sup>&</sup>lt;sup>11</sup> Simon, Stephanie. "To Replace Oil, U.S. Experts See Amber Waves of Plastic." The Los Angeles Times, June 26, 2005.

fruit, herbs, and brussels sprouts in November 2005. A few weeks later, Wal-Mart also added the new packaging for cut vegetables, bread bags, donut boxes, and gift cards. Replacing 114 million plastic containers a year with PLA varieties saves about 800,000 barrels of oil annually.

 Additional companies include the following: Lees Carpets; Milliken and Company, textile manufacturer, Quaker Fabric Corp., and Valdese Weavers.

NatureWorks sales continue to grow steadily. Sales in 2006 more than doubled from 2005. The company projects another 30 to 40 percent growth in 2007. They are doing everything they can to increase capacity and expect to have new capacity come online in mid-2008. As of 2006, NatureWorks was shipping PLA resin in bulk to customers who manufacture it into packaging materials, clothing, and fiber for apparel, carpeting, and bedding products. The technology to control the behavior of PLA in applications that need higher heat resistance, such as fibers for clothing, carpet, industrial use, packaging films, and certain kinds of containers, was developed under the ATP-funded program.

The ATP-funded technology has led to new U.S. jobs, reduced petroleum consumption by 14-16 million barrels, and reduced greenhouse gases by nearly 2 million metric tons. For every dollar of ATP investment, the nation will receive approximately \$11-24 in cost savings. The project's net present value is estimated at \$21-50 million. In addition, the biorefining process NatureWorks uses to produce lactic acid and PLA has the potential to enable future additional "green" applications, such as chemicals, solvents, additives, catalysts, biofuels, and specialty chemicals.

#### Conclusion

Cargill, Inc. wanted to improve the properties of renewable resource-based plastics called polylactic-acid–based polymers (PLA) to reduce dependence on petroleum and reduce waste in landfills. Furthermore, they wanted to gain market share in Europe and Asia, where environmental regulations make biodegradable plastics highly desirable. Cargill sought out Dow Chemical for its experience in the plastics industry. The two companies formed a joint partnership in 1997, called Cargill Dow Polymers LLC (CDP), near the end of the ATP-funded project.

Cargill, and later CDP, made significant improvements in PLA deficiencies over the course of the project, such as improved heat resistance. However, they were not able to lower the cost enough to attract U.S. customers in large numbers by the end of the project. The European and Asian markets caught on first, because these consumers respond more to the appeal of making and using plastics from a renewable resource. Also, composting and recycling regulations in Europe and Asia push market demand higher. Nevertheless, the U.S. market is growing as PLA costs relative to petroleum-based plastics have declined. Cargill bought Dow's share of CDP in 2005 and renamed the company NatureWorks.

As of 2006, NatureWorks was delivering PLA resin in bulk to hundreds of customers worldwide who then convert the resin into packaging for food and other items, clothing, carpeting, fiber, and bedding products. The PLA product has won five awards and four patents and has led to numerous articles and presentations.

Pelsoci, Thomas, ATP-Funded Green Process Technologies: Improving U.S. Industrial Competitiveness with Applications in Packaging, Metals Recycling, Energy, and Water Treatment, GCR 06-897, February 2007. <a href="https://www.atp.nist.gov/eao/gcr06-897.pdf">http://www.atp.nist.gov/eao/gcr06-897.pdf</a>

**Project Title:** Improving Biodegradable Plastics Manufactured from Corn (Development of Improved Functional Properties in Renewable-Resource-Based Biodegradable Plastics)

**Project:** To explore ways to improve the thermal properties of polylactic-acid-based polymer (PLA), a corn-based biodegradable polymer that could replace some non-degradable plastics.

**Duration:** 2/1/1995-1/31/1998 **ATP Number:** 94-01-0173

#### Funding\*\* (in thousands):

ATP Final Cost \$1,910 51.7%
Participant Final Cost 1,784 48.3%

Total \$3,694

Accomplishments: Cargill sought to improve the properties of PLA resin (pellets) for producing a variety of corn-based plastic products using diverse manufacturing techniques: fibers, films, and thermoforming. They formed a joint venture with Dow Chemical called Cargill Dow Polymers LLC (CDP). They called the PLA resin "NatureWorks." The success of the ATP-funded technology enabled CDP to accomplish the following:

- CDP teamed with Purac, a natural lactic acid producer, to develop a low-cost supply of lactic acid. They built a semi-commercial lactic acid plant in Blair, Nebraska, in 1998 with an annual capacity of 34,000 metric tons.
- CDP optimized polymer blends, additives, and manufacturing techniques for a multitude of applications in food packaging and fibers, with a constant view to degradation/compostability.
- CDP enhanced the functional properties of PLA resins and reduced the hardening times of the products manufactured from 60 seconds to 8 seconds.
- In 2002, CDP opened a major manufacturing PLA plant in Blair, Nebraska that has the capability to produce 140,000 metric tons of PLA resin annually, consuming up to 40,000 bushels of corn daily.
- The company partnered with Wilkinson
   Manufacturing Company of Fort Calhoun, Nebraska
   to mold food containers and bedding products from PLA.

 In April 2003, CDP signed a master license agreement with Toray Industries Incorporated, one of the world's largest fiber and textile producers, with 12 manufacturing plants and 56 global subsidiaries and affiliates.

The Cargill-Dow partnership won the following awards:

- 2000 Innovation and Technology Award from Industry Week magazine
- 2001 Technology-of-the-Year Award from the Department of Energy's Office of Industrial Technologies
- 2001 Research and Development Innovation Award from Discover Magazine
- 2001 Design and Engineering Award from Popular Mechanics magazine
- 2002 U.S. Presidential Green Chemistry Challenge Award in the "Alternative Reaction Conditions" category

Researchers received the following patents for technologies related to the ATP-funded project:

- "Melt-stable semi-crystalline lactide polymer film and process for manufacture thereof" (No. 6,093,791: filed March 9, 1998, granted July 25, 2000)
- "Degradable polymer fibers; preparation product; and, methods of use"
   (No. 6,506,873: filed May 4, 1998, granted January 14, 2003)
- "Paper having a melt-stable lactide polymer coating and process for manufacture thereof" (No. 6,197,380: filed April 6, 1999, granted March 6, 2001)
- "Melt-stable semi-crystalline lactide polymer film and process for manufacture therof" (No. 6,121,410: filed July 27, 1999, granted September 19, 2000)

<sup>\*\*</sup>As of December 9, 1997, large single applicant firms are required to pay 60% of all ATP project costs. Prior to this date, single applicant firms, regardless of size, were required to pay indirect costs.

#### Commercialization Status: Cargill bought

Dow's share of CDP in 2005 and renamed the company NatureWorks (the name they had given the PLA resin product). As of 2006, NatureWorks sold eight distinct grades of PLA resin for food packaging:

- 2002D is used for cold-drink cups, blister packs, dairy containers, and transparent food containers based on processes called extrusion and thermoforming.
- 2100D is used for plates and bowls for hot food and microwavable trays by extrusion and thermoforming.
- 3001D is used for cutlery, cups, and plates by injection.
- 3051D is also used for cutlery, cups, and plates by injection molding.
- 4032D is used for laminating, to seal in flavors, and to resist grease and oil based on baxially oriented high-heat film.
- 4042D works well for candy twist wraps and similar applications using biaxially oriented film.
- 4060D for a heat seal layer used in combination with other PLA films.
- 7000D is used for bottles for dairy products and edible oils based on injection stretch blow molding.

NatureWorks sells these PLA resins to hundreds of manufacturers worldwide for fabrication into products. For example, Wilkinson Manufacturing was the first to use PLA plastic in its product, NaturesPLAstic. PLA is suitable for cold or room-temperature food packaging. Sample commercial partners are:

- Brenmar Company, authorized distributor of the NatureWorks PLA line of products, which includes the VersaPak clear packaging product line for deli, bakery, and produce. Brenmar also offers NatureWorks PLA products such as plates, cutlery, and cold-drink cups with lids (see http://www.brenmarco.com).
- Wilkinson Manufacturing, which produces clear food packaging under the brand name "NaturesPLAstic" (see http://www.wilkinsonindustries.com).

- Wild Oats Markets Inc., which offers PLA-based packages and composts them in a commercial facility.
- Coca Cola Company, which uses PLA soft drink cups.
- Wal-Mart, which produces food packaging that uses PLA. After testing PLA plastics for a year, the company introduced packaging for strawberries, cut fruit, herbs, and brussels sprouts in November 2005. Wal-Mart added the new PLA packaging for cut vegetables, bread bags, donut boxes, and gift cards soon after. Those products represent 114 million plastic containers a year, the equivalent of 800,000 barrels of oil.

In addition to food packaging, NatureWorks sells PLA pellets for fiber applications. Ingeo fibers (made from PLA) have been blended with other fibers to produce apparel, bedding, carpet, furnishings, and personal care products.

- Pacific Coast Feather Company, which manufacturers comforter and pillow fiber filling; their products are carried by Bed Bath and Beyond, Linens N Things, Marshall Fields stores, and others.
- Interface Flooring Systems, which produces a residential carpet product created from Ingeo.

**Outlook:** The outlook for PLA is strong. Asian and European markets for renewable-resource-based plastics continue to grow. For example, the Japanese eco-business market, which includes biodegradable plastics, is projected to grow from \$251 billion in 2000 to \$410 billion in 2010. European consumption of biodegradable polymers nearly doubled from 2001 to 2003, to approximately 40,000 metric tons per year. By 2004, European consumption of degradable plastics had reached 50,000 metric tons (\$145 million), with growth expected to reach 0.5 to 1 million metric tons by 2010 (\$1.4 to \$2.8 billion), or 10 percent of the total plastics market.

The U.S. market for degradable plastics reached 115,000 metric tons (\$330 million) in 2004. With annual growth projected at 13.7 percent, the market will reach 170,000 metric tons (\$490 million) in 2008; PLA's market share will be 36 percent. <sup>14</sup> NatureWorks sales in 2006 more than doubled from 2005. The company projects another 30 to 40 percent growth in 2007. They expect to expand capacity in mid-2008.

<sup>14 &</sup>quot;Degradable Plastics to 2008." Freedonia Group 2004, http://www.freedoniagroup.com/pdf/1866smwe.pdf.

#### Composite Performance Score: \* \* \* \*

**Number of Employees:** NatureWorks had 230 employees as of February 2005. NatureWorks was spun out of a large company, Cargill, Inc.

#### Company:

NatureWorks, LLC P.O. Box 9300

Minneapolis, MN 55440-9300 Contact: Chris Ryan Phone: (952) 742-0448

#### **Subcontractors:**

- University of Minnesota Minneapolis, MN
- Pennsylvania State University
   University Park, PA
- California Tech
   Pasadena, CA
- University of Tennessee Knoxville, TN
- Technology Management Group Detroit, MI
- Organic Waste Systems Dayton, OH
- Fiber Science
   Palm Bay, FL
- Scott Gessner and Associates Encinitas, CA
- Nangeroni and Associates Doylestown, PA

**Publications:** Researchers published a number of academic articles concerning PLA technology, as listed below:

- Thakur, Khalid A.M., Robert T. Kean, John M. Zupfer, Nancy U. Buehler, Matthew A. Doscotch, and Eric J. Munson. "Solid State 13C CP-MAS NMR Studies of the Crystallinity and Morphology of Poly(L-lactide)."
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